4 CONCEPTUAL MODEL OF COPPER AND NICKEL CYCLING

4.1 Introduction

Copper and nickel cycling is important in Lower South San Francisco Bay because it plays a major role in both the fate and toxicity of the metal loads that enter the estuary. Uptake, accumulation, and toxicity vary with the chemical forms of the metals, since only some species are bioavailable for uptake. Chemical speciation also influences fate and transport processes, since the dissolved metals can be complexed with organic ligands, and since only free ions are adsorbed to inorganic suspended particles. The adsorptive/desorptive exchange between dissolved metals and suspended particles may be an important source of dissolved copper and nickel during resuspension events. Cycling between the water and sediments is very important, since sediments contain much of the historical loads of copper and nickel. Copper and nickel cycling in South San Francisco Bay have been studied by Luoma and Phillips (1988), Kuwabara et al. (1989), Flegel et al. (1991), Donat et al. (1994), Sañudo-Wilhelmy et al. (1996), Rivera-Duarte and Flegel (1997), and Luoma et al. (1998). Sedlak et al. (1997) and Bedsworth and Sedlak (1999) have studied the speciation of copper and nickel in wastewater effluents and surface runoff entering the Bay.

The conceptual model for copper cycling is depicted in Figures 4-1 and 4-2, and in a parallel set of figures, the conceptual model for nickel cycling is presented in Figures 4-3 and 4-4. Two figures are presented for each metal to separately emphasize both water column and benthic processes. Due to the similarities in copper and nickel cycling, both metals are discussed together below.

All major trophic components are shown in the cycling figures (Figures 4-1 and 4-3) to indicate the trophic transfer of copper and nickel through the food web and the uptake and excretion interactions of these organisms with dissolved metals in the water. The higher trophic components and their associated processes have been shaded since they are not expected to play a major role in the biogeochemical cycling, and since copper and nickel accumulation and toxicity in fish, marine mammals, and birds has not been a documented problem in South San Francisco Bay. Phytoplankton are important to the cycling of copper and nickel, and zooplankton and benthic animals have a major influence on phytoplankton through their grazing activities. Phytoplankton and zooplankton (including bivalve larvae) are the most sensitive organisms to copper toxicity and are the major focus of the impairment assessment. Biomagnification through the food web is not a concern with copper and nickel.

4.2 Abiotic Cycling

4.2.1 Copper and Nickel Speciation

Both copper and nickel enter Lower South San Francisco Bay through point and nonpoint source discharges, and are present either in the form of colloidal or dissolved species, or associated with particulate material. Colloidal species are not thought to be important for Lower South San Francisco Bay (Sañudo-Wilhelmy et al., 1996). Dissolved species consist of the free ion,

inorganic complexes, and organic complexes. Based on the work of Sedlak et al. (1997), who examined the complexes of copper and nickel in the effluents of the three wastewater treatment plants and in two surface streams that discharge into Lower South San Francisco Bay, the organic ligands complexed with the metals range from moderately strong complexing ligands, such as humic substances, to extremely stable complexing ligands comparable to synthetic chelating agents. More recent work of Bedsworth and Sedlak (1999) identify nickel ethylene diaminetetrancetate as a major nonreactive nickel species in San Francisco Bay.

The particulate forms of copper and nickel are present as either metal adsorbed to upland sediments that erode and are transported in stream channels, adsorbed to solids that are discharged in wastewater, embedded in the matrix of soil particles at natural background levels, as copper-enriched particles that originate from brake pad use, or other minor anthropogenically related sources.

Normally, metal concentrations in the aqueous phase are quantified in terms of either total concentration or total dissolved concentration. Detailed speciation data are typically not available. However, an exception to this statement is found in the work of Sedlak et al. (1997), who did determine copper and nickel speciation in the samples they collected from the three wastewater effluent streams and from the two surface streams. First, in terms of the traditional dissolved and total concentration relationship, they found that a majority of the copper in the effluents of the San Jose and Palo Alto water pollution control plants (WPCPs) was dissolved, while about 30 percent of the copper in the effluent of the Sunnyvale WPCP was dissolved. Nearly all of the nickel was dissolved in all wastewater effluents. Thus, dissolved metal concentrations in wastewater effluents that enter into Lower South San Francisco Bay typically exceed the particulate concentration. In the surface streams, however, the percentage of copper and nickel present in particulate form was nearly always higher than in the wastewater (about 30 to 60 percent of the total concentrations).

The copper and nickel organic complexes characterized by Sedlak et al. (1997) revealed that relatively high concentrations of copper and nickel complexes associated with strong ligands were measured in both wastewater effluents and in the surface stream samples. Somewhat higher percentages of these stable complexes were associated with wastewater effluents. The implication of these findings is that, since stable complexes are not likely to be bioavailable, they could be flushed out of Lower South San Francisco Bay before the complexes dissociate. Furthermore, if these stable complexes are present in wastewater effluents at higher concentrations than in nonpoint sources, as suggested by Sedlak et al. (1997), then equal reduction in concentrations and loadings from these differing source types could result in different levels of copper and nickel in biological organisms. Other researchers (e.g., Donat et al., 1994) have also documented the importance of metal-organic complexes in San Francisco Bay. More recently, Bedworth and Sedlak (1999) discuss the possibility that the unreactive forms of the metals could dissociate into more bioavailable forms when mixed with seawater, although the dissociation rates may be small for copper and nickel.

Once copper and nickel enter the Bay, their chemical forms change as a result of the different master variables that control speciation, such as pH, dissolved organic carbon concentrations, oxidation-reduction potential, salinity, affinity of metals for particulates (especially particulates

that contain amorphous iron), and biologically related processes (discussed in the next section). Furthermore, if concentrations of copper and nickel are high enough, precipitation of one or both of those metals can occur. However, at the concentrations present in Lower South San Francisco Bay (dissolved copper concentrations less than 10 μg/L, and dissolved nickel concentrations less than 15 μg/L; see Section 6), precipitation is not likely to occur, and therefore precipitation is not likely to influence the concentrations of copper and nickel in the Bay.

Some speciation reactions are fast, and can be thought of as equilibrium processes (such as speciation between inorganic forms), while other reactions may be slower and can be kinetically limited (dissociation of stable metal-organic ligands, for example). Depending on the relationship between flushing time in Lower South San Francisco Bay and the rate of decomposition of the stable organic complexes, those complexes might be transported out into Central South San Francisco Bay, or even into the Pacific Ocean, before significant dissociation occurs.

The major inorganic and organic species for copper and nickel in Lower South Bay are shown in Figures 4-1 and 4-3, respectively. The major inorganic ligands available are those most prevalent in diluted Pacific Ocean water that eventually enters and resides in Lower South San Francisco Bay. Those ligands are primarily chloride, sulfate, hydroxide, and carbonates or bicarbonates (Donat et al., 1994). The concentrations of the available ligands change from the dry to the wet season, as well as from the near-shore regions to the main Bay regions. Salinities in the sloughs can be as low as several practical salinity units (psu), and salinities in the Bay can vary from about 10 to 15 psu to near sea water at about 34 psu. Due to the abundance of inorganic ligands, and the affinity of the copper and nickel for those ligands, it is likely that inorganic complexes such as $NiCO_3$ or $Cu(OH)_2$ are present in greater concentrations than are the free ions Ni^{++} or Cu^{++}, although the relative abundance of inorganic species can differ from study to study (Donat et al., 1994). Depending on the bioavailability of the inorganic complexes compared to the free ions, the higher salinity waters may help to control the concentration of bioavailable copper and nickel. Specific calculations of inorganic species distribution related to South San Francisco Bay are shown in Appendix A. Two alternative abiotic cycling diagrams of copper and nickel are also shown there. The simpler diagrams (see Figures A-3 and A-4), which requires fewer data to implement, may not accurately portray the rate-limited reactions with L_1-ligands. For that reason, this simplified cycling model is less preferred, assuming the appropriate rate constants to implement the more sophisticated approach can be generated during the project.

4.2.2   Sorption Processes

Copper and nickel in the water column can adsorb to particulate matter, and thereby provide an important linkage to the sediment cycle. Some of the highest suspended sediment concentrations in San Francisco Bay are present in Lower South San Francisco Bay, as shown in Section 6 of this report. Also at locations in Lower South San Francisco Bay, a major fraction of the total copper and nickel present in the water column is associated with particulates (see also Section 6).

The major inorganic species that are thought to participate in the adsorption process are the free ions Cu^{++} or Ni^{++} (Wood et al., 1995). Some evidence is provided by Wood et al. that the adsorption-desorption process is kinetically limited, although the result is not conclusive. Often, adsorption-desorption processes are treated as equilibrium processes since they typically occur

quickly. If the process is kinetically limited, then copper or nickel discharged in dissolved form would not be in equilibrium with the particulate or adsorbed metal, but would exceed equilibrium concentrations at locations closer to discharge points, and approach equilibrium concentrations at locations farther from discharge points. In Appendix B, estimates of adsorption and desorption fluxes are provided that appear to show rates of desorption exceed rates of adsorption.

To illustrate the importance of adsorption to sediments, Tables 4-1 and 4-2 have been prepared which show the association of copper and nickel with sediments. These calculations are only approximate, since they assume equilibrium partitioning. However, they do illustrate useful concepts. Note that in the water column, copper and nickel concentrations of particulates are higher typically than in bedded sediments. This could indicate that finer particle sizes are present in the water column than in the bed. Furthermore, concentrations in particulates generally increase with distance up the Bay, illustrating a further particle size effect: smaller particles are transported up-bay. The hypothetical partition coefficient likewise increases, in the up-bay direction.

4.2.3   Sediment Processes

The sediment is an environment that influences the speciation of both copper and nickel in ways that differ from the water column (see Figures 4-2 and 4-4). A major difference between the water column and sediments is the likelihood that the oxidation-reduction potential is lower in the sediments. In the water column, dissolved oxygen is typically present at concentrations that indicate an oxidizing condition. Thus, copper is likely to be present there as $Cu(II)$ species, even if $Cu(I)$ species are discharged into the Bay. Nickel is also likely to be present as $Ni(II)$ species, but nickel is not sensitive to oxidation-reduction reactions. However, oxidation-reduction conditions are likely to change to become more reducing with increasing depth into the sediments, as Figures 4-2 and 4-4 indicate. Data from the San Francisco Estuary Institute (SFEI) database show Eh values in the top 5 centimeters (cm) of bedded sediments are typically –20 to –60 millivolts (mV), suggestive of mildly reducing conditions. When conditions begin to favor a reducing environment, the copper is reduced to $Cu(I)$ species, while nickel remains unaffected. Additionally, major constituents in the water column, such as nitrate or sulfate, can also be reduced in the sediments to form ammonia and sulfides, respectively.

Often, copper concentrations in a reducing environment can be controlled by solubility. For example, copper sulfides may precipitate, and cause dissolved concentrations of copper in the sediments to decrease, although the total concentration that would be measured in the sediments may not be appreciably affected. However, reduced copper can also form complexes with chlorides and reduce the possibility of solubility being exceeded. Although nickel is not reduced in the sediments, it can complex with sulfides and also possibly precipitate, and thereby have a solubility control exerted as well.

The processes described above that tend to reduce soluble copper and nickel in the sediments can be offset by other processes. Living organisms on or within the sediments, such as worms or bivalves, can bioturb the sediments, and provide preferential pathways for copper or nickel to be diffused and advected back into the Bay waters, and consequently alter the oxidation-reduction potential. Not only can organisms such as bivalves provide preferential pathways, but they can

also bioirrigate the sediments by pumping water as they feed. Also, Rivera-Duarte and Flegal (1997) discuss the importance of degradation of organic matter at the sediment-water interface, release of metals from manganese oxyhydroxides, and release of metals as soluble metal-sulfide complexes as mechanisms that tend to enhance metal concentrations in or at the surface of bedded sediments.

Although the processes that influence the fate of copper and nickel in the sediments are complex and not completely understood, nevertheless estimates of soluble flux exchanges between the water column and sediments are small compared to other fluxes (between one and two orders of magnitude less than other fluxes). Previous estimates were provided in the Source Characterization Report (URS Greiner Woodward Clyde, 1998). In Appendix C of this report, simplified calculations are also provided, which assume a steady-state diffusion flux into the water column. Based on these results, it is possible that the sediments can be modeled as a "black box," with a prescribed soluble flux into the water column. This will prevent unnecessary focus on generating a mechanistic representation of the flux. Based on present knowledge, the focus should be on exchange of particles instead.

4.2.4 Transport Processes

A brief summary of copper and nickel transport is presented here, while a discussion of the primary forcing functions (tides, winds, meteorologic events, hydrology, and bathymetry) are discussed more completely in Section 5. An overview of how those processes are manifested to induce copper and nickel transport is emphasized.

The transport of copper and nickel within, and out of, Lower South San Francisco Bay behaves differently in the dry and the wet seasons. During the dry season, which typically begins in May and continues through October, local precipitation is minimal, and natural surface stream flows greatly diminish or cease altogether. The remaining freshwater discharges during the dry season are from the three wastewater discharges, which together discharge approximately 155 mgd (240 cubic feet per second [cfs], or 6.8 m^3/s). During the dry season, evaporation can be significant relative to the wastewater inflow rates. Evaporation rates in the dry summer season are on the order of 0.5 inches/day at the Tracy Pumping Station. Based on an approximate surface area of Lower South San Francisco Bay equal to 4 x 10^7 m^2, the dry season evaporation rate can be on the order of 145 mgd (220 cfs, or 6.3 m^3/s). Because freshwater discharges and evaporation are nearly the same, the benefits of the wastewater discharges in enhancing flushing during the dry season may be negated.

During the dry season, the primary transport-inducing mechanisms are tidal, wind, and water density gradients (Gross, 1997). Of these three, tidal-induced transport predominates.

Gross (1997) also estimated residence times of solutes introduced into Lower South San Francisco Bay during the dry season. The release of solutes from three wastewater dischargers was simulated with a mathematical model. The residence times pertain only to conservative solutes that do not decay or interact with other constituents, or with the sediments. He estimated the residence times using both two-dimensional and three-dimensional models. The three-dimensional model results are reported first, and are based on more realistic modeling assumptions. For the case where the three major transport-inducing mechanisms were simulated,

the residence times ranged from 13 days for the Palo Alto discharge to 20 days for the San Jose discharge. These residence times are less than estimates made either using two-dimensional modeling by Gross (62 to 67 days) or estimates of 40 to 65 days made by Smith and Gross (1997), or estimates of 40 to 70 days made by Walters et al. (1985).

Transport during wet weather conditions in Lower South San Francisco Bay has been less well studied. The relative importance of various transport-inducing conditions is different from dry weather conditions. Periodically, during the wet season, large amounts of surface water discharges directly into the Bay, precipitation falls directly on the Bay, evaporation is reduced, and Delta discharges are large. Density-driven transport might be very important during the wet season (depending on the severity of the wet season), particularly since a relatively deep channel is present throughout the Bay, and extends into Lower South San Francisco Bay. Dense saline water can intrude into the Bay through this channel and produce a complicated flow pattern of current speeds and directions, both spatially (over depth and horizontal location) and over time. The shallow portions of the Bay, outside of the channel, are not as likely to exhibit a strong vertical density stratification. Although transport of solutes in Lower South San Francisco Bay has been described in terms of a dry and a wet season, transitions between seasons link the dry season with the wet season. Following a very wet year, for example, salinities in South San Francisco Bay can remain low into the dry season.

4.3   Biological Cycling and Food Web Accumulation

The biological portion of the conceptual model includes the effects of organisms on the cycling of copper and nickel in the water and sediments and the accumulation of the metals in the food web. The food web shown in Figures 4-1 and 4-3 is divided into six trophic components: producers, zooplankton, benthos, nonpiscivorous fish, piscivorous fish, and higher trophic level organisms such as marine mammals and birds. These represent the major feeding pathways for trophic transfer and food web accumulation of toxicants in the Bay. The higher trophic components and their associated processes have been shaded since they are not expected to play a major role in the biogeochemical cycling, and since copper and nickel accumulation and toxicity in fish, marine mammals, and birds has not been a documented problem in South San Francisco Bay. Phytoplankton are important to the cycling of copper and nickel, and zooplankton and benthic animals have a major influence on phytoplankton through their grazing activities. Phytoplankton and zooplankton (including bivalve larvae) are the most sensitive organisms to copper toxicity and are the major focus of the impairment assessment.

4.3.1   Organism Effects on Biogeochemical Cycling

Aquatic organisms influence the biogeochemical cycling of copper and nickel through uptake and excretion processes, incorporation into biological tissues, and production of organic detrital material containing the metals. Uptake removes dissolved metals from the water column and incorporates them in the biota, while excretion returns metals back to the water in soluble forms. However, this biological processing can change the form and bioavailability of the metals. Free metal ions and weak complexes with inorganic species are the forms that are most readily assimilated from the water, while excreted forms may be complexed with organic ligands that are much less available for uptake. In addition, phytoplankton excrete cellular exudates that chelate copper ions, effectively reducing copper bioavailability and toxicity (McKnight and Morel, 1979; Van den Berg et al., 1979).

Uptake removal fluxes of copper and nickel from the water depend on the product of the uptake rates, bioavailable metal concentrations in the water, and organism densities. Excretion fluxes depend on the product of the excretion rates, metal concentrations in the organisms, and organism densities. Since microbial organisms and phytoplankton typically have higher uptake and excretion rates than higher trophic levels (due to their high surface-to-volume ratios and high metabolic activities), they are more important for the biogeochemical cycling of metals than the higher trophic levels.

Food web processing produces particulate organic detrital forms of copper and nickel in fecal material. This includes the fraction of the metals in food items that are not assimilated during digestion and passage through the gut, as well as previously assimilated metals that are eliminated in feces. These detrital organic forms settle and deposit the metals in the sediments. Plankton mortality and phytoplankton settling also contribute organic detrital metals to the water column and sediments. Some of these metals are cycled back to the food web through the detrital food chain. Others are released as soluble forms to the sediment porewaters and overlying water column as the organic material decomposes.

4.3.2   Importance of Biological Effects on Biogeochemical Cycling in South San Francisco Bay

The most important biological component of the biogeochemical cycles of copper and nickel in South San Francisco Bay is processing by the phytoplankton community. Phytoplankton are well known to control nutrient cycles in water, and could therefore be expected to have a significant effect on the cycling of nutrient metals. Phytoplankton remove dissolved copper and nickel from the water column through uptake processes. The removed metals are incorporated into algal cells, which settle to the sediments or are assimilated by algal and detrital consumers. The net effect is a reduction in dissolved water column concentrations of the metals, and an increase in organic particulate forms of the metals, most of which accumulate in the sediments before being regenerated and released. Phytoplankton uptake and regeneration play an important role in copper and nickel cycling in the oceans, and are thought to control the vertical concentration profiles of these metals in the upper portion of the water column (Bruland et al., 1991; Sunda and Huntsman, 1995). However, the importance of phytoplankton uptake in estuaries is less clear. Dissolved copper depletion during phytoplankton blooms has not been demonstrated in either South San Francisco Bay (Luoma et al., 1998) or in other estuaries (Slauenwhite et al., 1991). However, significant nickel removal, as well as reduction of other metals such as zinc and cadmium, was detected during a bloom in South San Francisco Bay (Luoma et al., 1998). This suggests that phytoplankton uptake of metals could be an important process. Lack of copper depletion could be due to other processes (e.g., significant copper sources) that exceed the magnitude of the phytoplankton uptake.

In estuaries, other metal fluxes such as external loads, sediment diffusion, and suspended particle exchange during resuspension events may be larger than phytoplankton uptake fluxes. If the phytoplankton fluxes are small relative to other processes, then biological cycling effects can be removed from the fate and transport modeling. Biological cycling can then be modeled separately to predict food web accumulation of copper and nickel, if necessary (for example, if tissue-based criteria are adopted).

In order to assess the importance of biological cycling, phytoplankton uptake removal fluxes were estimated for copper and nickel, both during blooms when maximum fluxes would occur, and averaged throughout the year. These fluxes were then compared to the loads and other major physical and chemical fluxes to determine if biological cycling can be decoupled from the fate and transport modeling. Uptake fluxes were calculated using the product of measured phytoplankton growth fluxes and estimates of the metal concentrations in phytoplankton cells. Unfortunately, copper and nickel concentrations have not been directly measured in San Francisco Bay phytoplankton, since the phytoplankton cannot be separated from the inorganic suspended particles that dominate the particulate material. Therefore, estimates were made from other sources in the literature that considered metal speciation and free ion concentrations. This allowed the results to be more readily extrapolated to South San Francisco Bay, since the speciation has been previously characterized by Donat et al. (1994).

4.3.2.1 Phytoplankton Growth Fluxes

During phytoplankton blooms in South San Francisco Bay, the peak algal concentrations range from 40 to 60 µg/l chlorophyll *a* (Cloern, 1996; Luoma et al., 1998). Assuming chlorophyll *a* is about 1% of the dry weight biomass, and a typical growth rate during a bloom is 2.0 per day, the maximum phytoplankton growth flux (product of growth rate and algal density) is 10 g dry wt/m^3-day. Note that this flux would occur only for short periods during the peak of the bloom.

The annual net primary production in South San Francisco Bay is about 12.5 mol C/m^2-yr (Cole and Cloern, 1984; Luoma et al., 1998). Assuming that carbon is about 50% of the dry weight biomass and that the average depth of the Lower South San Francisco Bay is 2.6 m, the annual average phytoplankton growth flux is 0.32 g dry wt/m^3-day. The annual average growth flux is about 3.2% of the peak flux during phytoplankton blooms.

4.3.2.2 Free Ion Concentrations

Copper and nickel uptake rates, and therefore cellular concentrations of the metals, are functions of the free ion concentrations of the metals. Free ion concentrations were estimated for the average copper and nickel concentrations in the Lower South San Francisco Bay (Figures 2-2 and 2-4) using the speciation results of Donat et al. (1994) to estimate the total inorganic species, and the geochemical model MINTEQ to estimate the inorganic complexation and free metal ion concentrations. In South San Francisco Bay, the inorganic copper species are 8 to 20% of the total dissolved copper, and the inorganic nickel species are 50 to 66% of the total dissolved nickel (Donat et al., 1994). The midpoints of these ranges, 14% and 58%, respectively, are used in the calculations below.

The average total dissolved copper concentration in Lower South San Francisco Bay is 3.3 µg/l during the dry season and 2.4 µg/l during the wet season. Assuming 14% of the total dissolved copper is present as free ion and inorganic copper species, the concentrations of the inorganic species are about 0.46 µg/l and 0.34 µg/l during the dry and wet seasons, respectively. Based on MINTEQ model calculations, about 4.8% of the inorganic species is free copper ion during the dry season and about 2.3% is free ion during the wet season. Therefore, the free copper ion concentrations are approximately 0.022 µg/l and 0.0077 µg/l during the dry and wet seasons, respectively.

The average total dissolved nickel concentration in Lower South San Francisco Bay is 3.8 µg/l during the dry season and 2.9 µg/l during the wet season. Assuming 58% of the total dissolved nickel is present as free ion and inorganic nickel species, the concentrations of the inorganic species are about 2.2 µg/l and 1.7 µg/l during the dry and wet seasons, respectively. Based on MINTEQ model calculations, about 15% of the inorganic species is free nickel ion during the dry season and about 8% is free ion during the wet season. Therefore, the free nickel ion concentrations are approximately 0.33 µg/l and 0.13 µg/l during the dry and wet seasons, respectively. Free nickel concentrations are about 15 times higher than the free copper concentrations during the dry season, and about 17 times higher during the wet season.

4.3.2.3 Phytoplankton Metal Concentrations

The free ion concentrations in the Bay can be used in conjunction with the results of recent phytoplankton uptake studies that measure copper and nickel uptake rates and cellular metal concentrations as functions of the free ion concentrations. This information can be used to estimate the concentrations of the metals in Bay phytoplankton. Many earlier uptake studies report only total dissolved metal concentrations, so it is difficult to extrapolate the results to the field, where the speciation and bioavailability are different from the experimental conditions.

Sunda and Huntsman (1995) measured copper accumulation in three diatoms and a coccolithophorid at free copper concentrations spanning 4 orders of magnitude. The accumulation patterns were almost identical in three of the species. At the higher concentrations, algal copper concentrations increased slowly (less than a factor of 10 over 3 orders of magnitude of free copper ion) due to algal regulation of copper uptake (Sunda and Huntsman, 1995). Algal copper concentrations of 18 umol Cu per mol C were measured at a free copper ion concentration of about 10 pM (0.00064 µg/l), the upper concentration range of the experiments. Assuming that carbon is about 50% of the algal dry weight biomass, this corresponds to an algal copper concentration of 48 µg/g dry wt. Since the maximum free copper concentration in the experiments was more than an order of magnitude lower than the free copper in South San Francisco Bay, the algal copper concentrations in the Bay would be expected to be a few times higher than this, but less than an order of magnitude higher.

Knauer et al. (1997) measured copper uptake rates and cellular accumulation as a function of free ion concentrations for the green algae *Scenedesmus subspicatus*. Uptake rates and copper accumulation showed saturation relationships due to regulation of uptake at high copper concentrations. The free copper concentrations in the Bay are in the saturation portions of these curves. The measured algal copper concentrations under these conditions was 2.9 umol/g dry wt, which equals 180 µg/g dry wt.

Phinney and Bruland (1997) measured copper and nickel uptake in the coastal diatom *Thallasiosira weissflogii* using South San Francisco Bay water. Although the experiments were conducted for other purposes, copper and nickel levels were measured in the diatoms cultured in Bay waters as controls. The resulting copper concentration in the algae was about 0.20 nM, and the nickel concentration was about 0.25 nM, for an algal density of 3.1 x 10^6 cells/l. Assuming a cell volume of 250 µm^3 and a cell water content of 90%, the algal metal concentrations would be about 165 µg/g dry wt for copper and about 190 µg/g dry wt for nickel. The algal nickel

concentration is about 25% higher than the copper concentration. Although there is uncertainty in these values due to the assumptions made to estimate the cell biomass, these values seem reasonable for several reasons. First, the copper value is only 3.4 times greater than the values measured by Sunda and Huntsman (1995) at free copper concentrations that were 1 or 2 orders of magnitude lower than concentrations in the Bay. Second, it is only 10% lower than the values measured by Knauer et al. (1997) at similar free ion concentrations. Third, since South San Francisco Bay water was used, all factors affecting the speciation and bioavailability of the metals in the Bay are accounted for in the uptake estimates. Fourth, although growth dilution can potentially reduce metal concentrations in algae during periods of very high growth (e.g., during blooms) if the uptake rates are not high enough, the experiments conducted by Knauer et al. (1997) and Sunda and Huntsman (1995) were conducted during the exponential growth phase of the cultures, so they should represent concentrations during periods of maximum growth. Copper uptake rates were measured by Knauer et al. (1997) during exponential growth, and these uptake rates were high enough to produce algal copper concentrations of 180 µg/g at the free ion concentrations in South San Francisco Bay. Therefore, the above values estimated from Phinney and Bruland (1997) will be used to calculate the algal uptake fluxes of copper and nickel below. However, it should be emphasized that these are only estimates.

4.3.2.4 Copper and Nickel Uptake Fluxes

Uptake fluxes for copper and nickel are calculated as the product of the algal growth fluxes and the metal concentrations in the algae. Using the maximum and average growth fluxes of 10 g/m^3-day and 0.32 g/m^3-day and the algal metal concentrations of 165 µg/g copper and 190 µg/g nickel discussed above, the following estimates were made. During algal blooms, the peak uptake flux for copper is 1,650 µg/m^3-day and the peak uptake flux for nickel is 1,900 µg/m^3-day. Averaged over an annual growth cycle, the average uptake flux for copper is 52.8 µg/m^3-day and the average uptake flux for nickel is 60.8 µg/m^3-day. Assuming that the volume of the Lower South San Francisco Bay is 8.6 x 10^7 m^3, these fluxes can be converted to more convenient units of kg/yr to facilitate comparison with other processes. The resulting maximum uptake fluxes are 51,800 kg/yr for copper and 59,600 kg/yr for nickel. The annual average uptake fluxes are 1,660 kg/yr for copper and 1,910 kg/yr for nickel. Note that the maximum fluxes could only occur for very short periods during the peak of phytoplankton blooms, so it is misleading to express them on a yearly basis. However, this allows comparison with other fluxes, as discussed below, and it shows the maximum effect of phytoplankton to put their uptake fluxes into perspective.

Using the flux estimates summarized in Figures 2-3 and 2-5, the average algal uptake fluxes are 1.5 times the POTW loads for copper and 1.3 times the POTW loads for nickel. Therefore, the phytoplankton uptake fluxes are similar to the current POTW loads and are greater than the estimated sediment diffusion fluxes and atmospheric loads. The maximum uptake fluxes are very high, much higher than the annual average tributary or POTW loads. However, these maximum fluxes could occur only during very short periods, and they could be obscured by other event-driven fluxes, such as storm runoff and resuspension events, which are also very high during their respective events, but which are averaged in the annual flux estimates shown in Figures 2-3 and 2-5.

Luoma et al. (1998) studied metal uptake by phytoplankton during a bloom in South San Francisco Bay and noted that dissolved nickel, zinc, and cadmium were significantly decreased during the bloom, but that dissolved copper was not (copper increased by 20% during the bloom). They estimated that phytoplankton uptake could cycle about 60% of the annual POTW loads of nickel, zinc, and cadmium in South San Francisco Bay, and therefore concluded that phytoplankton were important in the biogeochemical cycling of these metals. However, since copper concentrations did not decrease during the bloom, they concluded that phytoplankton uptake was not important for copper.

Our estimates of the fractions of the nickel POTW loads processed by phytoplankton in the Lower South San Francisco Bay were about twice as high as those of Luoma et al. (1998). However, these values are not directly comparable, since they considered the whole South Bay (rather than the Lower South Bay), so the volumes and total loads were different. Their estimate of the algal uptake flux of nickel was 120,000 mol/yr for the whole South Bay, which when converted to a volumetric daily flux is about 15 µg/m^3-day. Our estimated flux of 60.8 µg/m^3-day is four times as high as that estimate. Our estimate could be high by a factor of 3 or 4, since this range brackets the results of the copper uptake studies used in our estimate of algal copper concentrations, which were in turn used to estimate nickel concentrations from the results of Phinney and Bruland (1997). Alternatively, the estimate of Luoma et al. (1998) could be low, since they estimated the uptake flux from the relative amounts of nickel and nutrient depletion in the water, and since a major resuspension event occurred during the bloom. Although dissolved nickel decreased 25% during the bloom, particulate nickel increased much more due to resuspension (Luoma et al., 1998). Therefore, resuspension could have released dissolved nickel into the water, masking part of the phytoplankton uptake. Resuspension and the associated release of dissolved metals could also explain why copper depletion was not detected during the bloom. However, regardless of the differences between our estimate and Luoma et al.'s (1998) estimate, both values are the same order of magnitude and indicate the importance of phytoplankton uptake on nickel cycling in the Bay.

More important is the discrepancy between our assessment of the importance of phytoplankton on copper. Although copper increased 20% during the bloom (Luoma et al., 1998), other processes such as wet season tributary loadings and metal release during resuspension could have masked the effects of phytoplankton uptake. These two processes make up about 90 % of the annual copper loads (Figure 2-3), in contrast to the POTW loads which are only about 8 % of the annual loads. In addition, the effects of these loads would have been higher during the spring phytoplankton bloom than indicated in the annual averages, since most of the tributary loads are confined to the wet season, and since the resuspension fluxes occur during discrete resuspension events. Such an event was observed during the bloom (Luoma et al., 1998). Dissolved copper concentrations may have increased more than nickel during resuspension due to more rapid desorption kinetics from the suspended particles. Resuspension and tributary loading could have also masked much of the nickel uptake by phytoplankton, although some depletion was still observed. If phytoplankton uptake is important for nickel and several other metals, then it should also be important for copper unless copper does not accumulate in the phytoplankton. This could occur only if the phytoplankton uptake kinetics are much slower for copper than for nickel, or if phytoplankton excretions of organic ligands during the bloom are so strong and abundant that they bind most of the dissolved copper and make it unavailable for uptake. Either

of these could result in significant growth dilution, rather than copper assimilation, during periods of rapid growth. However, the uptake studies by Knauer et al. (1997) suggest that phytoplankton uptake rates for copper are high enough to support higher cellular concentrations than the values used in our estimates, even during periods of maximum growth. In addition, the results of Phinney and Bruland (1997) indicate that copper concentrations in phytoplankton cultured in South San Francisco Bay water are only about 25% lower than nickel concentrations, and these estimates include the effects of speciation and bioavailability of both metals. Even if algal excretion of organic ligands were sufficient to prevent significant copper uptake during blooms, they would not be sufficient to prevent uptake throughout the year based on the existing information on ligand concentrations and copper bioavailability in the South Bay (e.g., Donat et al., 1994). Therefore, our results suggest that if phytoplankton uptake is important for nickel, it is reasonable to assume that it could also be important for copper.

Although there is some uncertainty in the phytoplankton uptake fluxes calculated above, the results indicate that phytoplankton effects on biogeochemical cycling can be important, and should therefore be included in the fate and transport modeling. In addition to their effect on metal removal from the water, phytoplankton blooms can also affect copper speciation and bioavailability through the release of organic compounds during blooms and bloom senescence (Sanders and Riedel, 1993). These effects should also be considered in the fate and transport modeling.

4.3.3   Phytoplankton Uptake and Toxicity

Phytoplankton uptake and toxicity from copper and nickel exposure are extremely important in Lower South San Francisco Bay for several reasons. Phytoplankton are among the most sensitive organisms to copper toxicity, and phytoplankton form the base of the food web and therefore support all of the higher trophic levels. Phytoplankton accumulation of metals is the major route of entry into the rest of the food web. Phytoplankton uptake also influences the biogeochemical cycling of the metals.

Figure 4-5 summarizes the important processes involved in the uptake and toxicity of copper in phytoplankton. The same general concepts also apply to nickel. Many of these concepts also apply to higher trophic level organisms, since they describe the general processes of metal accumulation in cells. However, the details of metal accumulation in cells have been studied more thoroughly for phytoplankton than for other aquatic organisms, since they are single cellular organisms, they are relatively easy to culture, and they are subject to uptake only from water, not food. Uptake and toxicity in higher trophic level organisms are typically studied at the whole body or tissue level, and they are complicated by simultaneous exposure to food and water uptake.

4.3.3.1 Uptake Mechanisms and Bioavailability

Copper, nickel, and other metal ions are transported into phytoplankton cells by transport proteins on the cell membrane. These proteins carry the metals across the cell membranes and release them into the cytoplasm. The receptor sites on the transport proteins compete with binding sites on suspended particles (adsorption) and organic and inorganic ligands for free metal ions. Depending on circumstances, uptake and toxicity depend on the concentration of either the free metal ion or the sum of the free ion and labile inorganic complexes. In this report,

we refer to these forms as the bioavailable forms of the metals. Metals complexed to strong organic ligands or adsorbed to suspended particles are not available for uptake since they cannot cross the cell membrane. However, these metals are still ultimately available to the system since complexation/dissociation reactions and adsorption/desorption reactions continually exchange free ions with the solution.

Copper and nickel uptake rates, cellular concentrations of the metals, and toxic effects are functions of the free ion concentrations of the metals. The free ion is a measure of the bioavailability of a metal, and shows better correlation with uptake and toxicity than the previously used total dissolved metal concentrations. However, the free metal ions are not necessarily the only bioavailable or toxic forms. For a particular salinity or water quality conditions, the free ion is proportional to other species such as labile inorganic complexes that may also be bioavailable. Therefore, the sum of all inorganic species should have the same correlation with uptake and toxicity as the free ion concentration. However, the free ion is currently more useful for assessing uptake and toxicity since uptake rates and toxic effects have been correlated with free ion concentrations in several recent studies.

In South San Francisco Bay, 8 to 20 percent of the dissolved copper and 50 to 66 percent of the dissolved nickel occurs as inorganic (and weak organic) complexes and free metal ions (Donat et al., 1994). The rest of the dissolved copper and nickel are complexed with strong organic ligands. Two classes of ligands have been identified for the metals, one representing very strong complexes, and another representing moderately strong complexes (Donat et al., 1994; Sedlak et al., 1997). The majority of dissolved copper in South San Francisco Bay is bound to the weaker of the two ligands that complex with copper, while almost all of the complexed nickel is associated with the strong ligand that complexes with nickel (Donat et al., 1994; Bedsworth and Sedlak, 1999).

Phytoplankton uptake and toxicity of copper and nickel are strongly influenced by water quality factors such as pH, alkalinity, hardness, dissolved organic matter, and suspended particulates, which affect the speciation and bioavailability of the metals. These variables determine the degrees of dissociation, complexation, and adsorption to particles, and therefore the availability of free metal ions and labile inorganic complexes, as well as competition with other cations for uptake sites on the cell membranes. In general, uptake rates and toxicity decrease with increases in any of these variables. The same general patterns are also seen in all other types of aquatic organisms.

Metal uptake rates in phytoplankton depend on both the concentration of metal bound to the uptake sites and the rate of transfer across the cell membrane. The metal concentration at the uptake sites depends on the bioavailable metal concentrations in the water and the metal binding affinity of the transport sites. Since the number of membrane transport sites on a cell is generally fixed, the uptake rates reach maximums when all sites are saturated. This produces the typical saturation relationships for metal uptake rates as functions of concentration in water.

4.3.3.2 Uptake Regulation

Metals are generally taken up by nutrient metal transport systems (Sunda and Huntsman, 1998). Since phytoplankton have specific nutrient requirements, they have cellular feedback

mechanisms which allow them to regulate intracellular metal concentrations to levels that are optimal for growth and metabolism. This is accomplished by reducing their uptake rates when intracellular concentrations start to become excessive. The number of membrane transport proteins and their metal affinities are generally fixed, so uptake rates are regulated by controlling the transport rates across the cell membrane (Sunda and Huntsman, 1998). These transport rates are adjusted by feedback controls within the cell that regulate the activity of the membrane transport proteins in response to intracellular metal concentrations (Sunda and Huntsman, 1998). However, this control has a limited capacity, so excessive metal accumulation and resulting toxicity will occur when the capacity is exceeded. This results in the typical sigmoidal relationships of cellular metal accumulation with increasing metal concentrations in water (Sunda and Huntsman, 1998). Cellular metal concentrations increase with increasing bioavailable metal concentrations in water over the lower concentration range, then level off to much slower rates of increase as uptake rates become regulated, and finally increase at a faster rate as the regulatory capacity is exceeded. Regulation of copper accumulation also occurs in aquatic invertebrates and fish (Sorensen, 1991; Borgmann et al., 1993).

4.3.3.3 Competitive Interactions with Other Metals

The metal transport proteins on the cell membranes are designed to bring nutrient metals into the cells. However, they are not entirely specific to single metals, so other metals with similar physicochemical characteristics can enter the cell through the same transport system. This produces competition for uptake sites between different metals in the water. This competition also extends further to processes within the cell, for example, to competition for binding sites on metalloproteins, or on intracellular control sites that regulate the activity of the membrane transport proteins (Sunda and Huntsman, 1998). Therefore, uptake rates could be reduced both by the presence of competing metal ions external to the cell (competition for binding sites on the membrane), as well as by the accumulation of competing metals inside the cell, which further reduces uptake rates through feedback control of transport kinetics at the cell membrane (Sunda and Huntsman, 1998).

Competitive interactions can be toxic or protective, depending on the circumstances. For example, high copper concentrations could reduce the uptake of a critical nutrient metal, such as manganese, producing growth inhibition due to manganese nutritional deficiency. On the other hand, high manganese concentrations could inhibit copper uptake and prevent copper toxicity at copper concentrations that would normally be toxic. This situation could currently be occurring in South San Francisco Bay (Bruland, personal communication, 1999). Competitive interactions with copper are known to occur between manganese, zinc, and iron (Sunda and Huntsman, 1998). Competitive interactions also occur with nickel but they are less well known.

4.3.3.4 Toxicity

Toxic effects on phytoplankton are typically measured in terms of reductions in growth rates. Therefore, toxicity can be produced both by nutritional deficiencies in competing nutrient metals, and by the accumulation of excess toxic metals, which disrupt the normal metabolism of the cell. Toxicity from excess metals can occur through the displacement of other nutrient metals from their metabolic sites, through substitution in critical metalloproteins, which disrupts their metabolic functions, or through other toxic mechanisms. Excessive concentrations of several metals typically increases toxicity through additive effects if the modes or sites of toxic action

are similar, or through increased stress to the phytoplankton cell even if they are not similar. However, as discussed above, competitive interactions can sometimes reduce toxicity by reducing uptake of a metal that would otherwise be toxic.

Phytoplankton have three major mechanisms for reducing toxicity when exposed to excessive concentrations of toxic metals such as copper and nickel. First, they produce phytochelatin, which binds the metals inside the cells and stores them in a nontoxic form (Ahner and Morel, 1995; Ahner et al., 1995). Second, some phytoplankton excrete organic cellular exudates at elevated copper concentrations, which chelate copper ions surrounding the cell, reducing copper bioavailability and uptake rates (McKnight and Morel, 1979; Van den Berg et al., 1979). Third, efflux systems are induced in some phytoplankton when intracellular metal concentrations become elevated to actively excrete accumulated metals from the cells (Sunda and Huntsman, 1998). However, all of these mechanisms have a limited capacity for detoxification, so toxic effects will occur when their capacity is exceeded. In addition, these detoxification pathways can sometimes reduce intracellular concentrations of competing nutrient metals, resulting in nutrient deficiencies from these other metals (Sunda and Huntsman, 1998).

4.3.4   Food Web Accumulation

Accumulation of copper and nickel in aquatic food webs depends on uptake from two routes of exposure, water and food. For the primary producers and bacteria, water is the only source of uptake, while for aquatic animals, food and water are both potentially important. For birds and marine mammals, food is the primary source of uptake, although dermal exposure to water also occurs. However, waterborne uptake from dermal exposure should be very small in comparison to uptake across the gills of aquatic animals, since large volumes of water are passed over relatively large respiratory surfaces in the gills.

The accumulation of metals from water depends on the relative rates of uptake, elimination, and growth dilution. The bioconcentration factor, which is the ratio of an organism's metal concentration to the water concentration (after equilibrium has been reached), is equal to the uptake rate divided by the sum of the elimination rate and growth rate. Growth acts similar to elimination in determining organism metal concentrations, since increases in tissue (or cell) mass dilute the metal concentrations. The rate at which equilibrium is reached depends on the elimination and growth rates. Since smaller organisms (lower trophic levels) typically have higher elimination and growth rates than larger organisms, they tend to reach equilibrium faster, and therefore respond much more rapidly to changes in water column concentrations.

Accumulation of copper and nickel from food depends on consumption rates, metal concentrations in foods, and assimilation efficiencies of the metals during digestion and passage through the gut. The trophic transfer factor, which is the ratio of the organism metal concentration to the concentration in its food supply (after equilibrium has been reached), is equal to the product of the consumption rate and metal assimilation efficiency from food divided by the sum of the elimination rate and growth rate. As with waterborne uptake, the rate at which equilibrium is reached depends on the elimination and growth rates. Elimination rates are often the same for waterborne and foodborne uptake (Reinfelder et al., 1998). The trophic transfer factor is an indicator of the biomagnification potential of the metal. Factors greater than 1 indicate magnification of metal concentrations between trophic levels. Food chain magnification

is not important for copper and nickel, although uptake from food may still be a major source of uptake and accumulation.

The total metal concentrations accumulating in aquatic animals depend on the sum of the bioconcentration component from water and the trophic transfer component from food. The waterborne component of accumulation is the product of the bioavailable metal concentration in water and the bioconcentration factor. The foodborne component of accumulation is the product of the metal concentration in food and the trophic transfer factor. Trophic transfer factors are calculated separately for each food item, using the corresponding food metal concentrations and consumption rates for each food type, and are summed to give the total foodborne contribution to accumulation.

Copper accumulation is regulated in many organisms (Sorensen, 1991; Borgmann et al., 1993). Copper is an essential micronutrient and performs numerous physiological functions. Biochemical pathways exist for efficiently extracting copper at low concentrations typical of uncontaminated environments, while at elevated exposure levels, homeostatic mechanisms exist to keep copper concentrations within a healthy range. This may occur through saturation of uptake pathways or copper binding sites in the organism, which limit uptake rates, or through the induction of detoxification pathways, which increase elimination. Fish tend to store excess copper in the liver and regulate accumulation in the muscle tissue (Sorensen, 1991). However, when copper concentrations in the environment become too high, the homeostasis mechanisms are overcome, and excessive copper can accumulate in all tissues. Less information is available on the nutritional importance of nickel, and whether or not it is regulated in aquatic organisms. The effects of nutrient metal regulation on uptake and elimination parameters must be considered in the calculations described above. Bioconcentration factors and trophic transfer factors are not constants, and they must be estimated in the context of site-specific exposure conditions.

The above model of food web accumulation represents a steady-state approach that describes equilibrium concentrations in organisms under constant metal exposure concentrations. Concentrations in producer organisms are estimated first, using bioconcentration factors and copper and nickel concentrations in the water. The metal concentrations in water must be adjusted to reflect only the bioavailable forms. Concentrations for herbivorous zooplankton are calculated next, using the same approach as for phytoplankton to estimate waterborne uptake in the zooplankton, and then adding the foodborne component of uptake. This is calculated from the trophic transfer factors and the phytoplankton metal concentrations calculated in the first step. This procedure is repeated for each successive link in the food web. For birds and mammals at the top of the food web, only foodborne uptake is considered. The above procedure estimates total metal concentrations in aquatic organisms, as well as indicating the relative contributions from water and food.

A kinetic approach could also be used to estimate temporal changes in organism metal concentrations resulting from seasonal fluctuations in water and sediment concentrations. This approach uses mass balance equations to describe the rates of change in organism metal concentrations due to waterborne uptake, foodborne uptake, elimination, and growth dilution. Fluxes are calculated for each of these processes using the same types of information used in the steady-state model. However, all of the fluxes are allowed to vary over time to reflect changing

metal concentrations in the water, food items, and consumer tissues, as well as seasonal variations in consumption rates, growth rates, and diet preferences. This approach would require the use of a computer simulation model. In general, phytoplankton and bacteria adjust to changes in metal exposure within a few hours or days, invertebrates within a few weeks or months, and fish within several months to a year or so. Again, these times depend primarily on the elimination rates of the metals in the organisms and on growth rates.

Bioconcentration factors and trophic transfer factors require the following types of information: uptake rates from water, depuration (elimination) rates, toxicant assimilation efficiencies from food, consumption rates, growth rates, and diet preferences. The last three items – consumption rates, growth rates, and diet preferences – can be estimated from the general biological literature. Uptake rates from water and depuration rates are reported in uptake/depuration experiments. If one of these parameters is known along with an experimentally determined bioconcentration factor or steady-state tissue concentration, then the missing parameter can be calculated. Toxicant assimilation efficiencies from food can be estimated from tissue accumulation measured in feeding experiments. Radiotracer techniques are also available to measure trace metal assimilation efficiencies.

4.4   Summary

1. Copper and nickel cycling is important in Lower South San Francisco Bay because it plays a major role in both the fate and toxicity of the metal loads entering the estuary.

2. The conceptual model of cycling involves chemical speciation of the metals and the chemical, physical, and biological processes that influence their fate, concentrations, and interactions between chemical forms. The species considered are the free metal ions; inorganic complexes with chlorides, hydroxides, carbonates, and sulfates; organic complexes with strong and weak ligands; and adsorbed forms and other particulate forms.

3. Speciation is very important since only free metal ions and labile inorganic complexes are available for uptake. Therefore, these are also the forms that determine toxicity. However, only a small fraction of the total copper and nickel in the water column occurs in these forms. Much of the dissolved copper and nickel is complexed with organic ligands, and particulate forms also represent a significant fraction of the total metal concentrations.

4. The inorganic copper species in South San Francisco Bay have been estimated to range from 8 to 20 % of the total dissolved copper, and the inorganic nickel species have been estimated to range from 50 to 65 % of the total dissolved nickel (Donat et al., 1994). However, this distribution could change as metal loads or ligand loads to the estuary change, or if other changes occur in the Bay that affect the internal cycling of the metals.

5. Complexation and adsorption are the are main processes that control copper and nickel speciation.

6. Inorganic complexation reactions are fast, and can be considered as equilibrium processes. Seasonal salinity variations have the largest effect on these reactions, since that determines the concentrations of the inorganic ligands that complex with the metals.

7. Organic complexation and sorption reactions are slower, and are considered to be kinetically limited. These slow kinetics may influence the fate and transport of the organic complexes and sorbed species in the estuary.

8. Adsorption processes are believed to depend on free metal ion concentrations.

9. Organic complexation reactions depend on the relative concentrations of organic ligands and dissolved metals. Two major classes of organic ligands have been identified in the South Bay, weaker ligands such as humic substances, and very strong ligands such as synthetic chelating agents (Donat et al., 1994; Sedlak et al., 1997; Bedsworth and Sedlak, 1999).

10. Bedsworth and Sedlak (1999) have identified EDTA as the major strong ligand for nickel in the South Bay, and have identified the source to be wastewater effluents. Almost all of the organically complexed nickel in the South Bay is associated with this strong ligand, while the weaker ligand class contains a major portion of the complexed copper (Donat et al., 1994; Bedsworth and Sedlak, 1999). The slow dissociation rates of these strong organic complexes may prevent speciation changes before the metals are transported out of the Lower South Bay.

11. Sediment processes are important in the speciation and cycling of copper and nickel. The redox conditions are lower in the sediments, producing different chemical reactions than occur in the water column.

12. Soluble fluxes between the water column and sediments are low compared to other sources of the metals. However, sediment resuspension and desorption may release large quantities of dissolved copper and nickel to the water column, making this a major source of dissolved metals.

13. The biological portion of the conceptual model includes the effects of organisms on the cycling of copper and nickel in the water and sediments, and the accumulation of the metals in the food web. Organisms influence biogeochemical cycling through uptake and excretion processes, incorporation into biological tissues, production of organic detrital material containing the metals, and subsequent metals release during decomposition and mineralization.

14. Uptake removes dissolved metals from the water column and incorporates them in the biota, while excretion returns metals back to the water in soluble forms. However, this biological processing can change the form and bioavailability of the metals. Free metal ions and weak inorganic complexes are the forms that are most readily assimilated from the water, while excreted forms may be complexed with organic ligands that are much less available for uptake. In addition, phytoplankton excrete cellular exudates that chelate copper ions, effectively reducing copper bioavailability and toxicity.

15. Particulate organic detrital copper and nickel are produced through food web processing. Following accumulation of the metals in the biota, processes such as phytoplankton settling,

plankton mortality, and egestion generate organic detrital metals that settle and deposit the metals in the sediments. These metals are released as soluble forms to the water column and sediment porewaters as the organic material decomposes.

16. The most important biological component of the copper and nickel biogeochemical cycles is processing by the phytoplankton.

17. In order to assess the importance of biological cycling, phytoplankton uptake removal fluxes were estimated and compared with the loads. Since phytoplankton metal concentrations are not available for the South Bay, they were estimated from uptake experiments in the literature using the free ion concentrations of copper and nickel in the South Bay. These values were used in conjunction with estimates of phytoplankton growth and productivity to estimate the metal uptake fluxes. Although there is some uncertainty in these estimates, the results indicate that phytoplankton processing is the same order of magnitude as current POTW loads into the Lower South Bay.

18. Although, significant copper depletion was not observed during a phytoplankton bloom in the South Bay, nickel and other metals were removed (Luoma et al., 1998). The algal fluxes could have been obscured by higher resuspension or wet season runoff fluxes which exceeded algal uptake during the bloom.

19. Phytoplankton uptake and toxicity from copper and nickel are extremely important in Lower South San Francisco Bay, since phytoplankton are among the most sensitive organisms to copper toxicity, and since phytoplankton form the base of the food web and therefore support all of the higher trophic levels. Phytoplankton accumulation of metals is the major route of entry into the rest of the food web, and phytoplankton uptake also influences the biogeochemical cycling of the metals.

20. Copper and nickel are taken up by nutrient metal transport proteins on the phytoplankton cell membranes. Since phytoplankton have specific nutrient requirements, they have cellular feedback mechanisms which allow them to regulate intracellular metal concentrations to levels that are optimum for growth and metabolism.

21. Only free metal ions and labile inorganic metal complexes are available for uptake, since metals complexed to strong organic ligands or adsorbed to suspended particles cannot cross the cell membrane. Water quality factors such as pH, alkalinity, hardness, dissolved organic matter, and suspended particulates influence the speciation and therefore uptake of the metals.

22. Competition with other metals can inhibit both copper and nickel uptake, as well as the uptake of other nutrient metals. This occurs through both competition for uptake sites on the cell membrane, as well as through intracellular sites that control membrane transport rates of the metals.

23. Toxic effects on phytoplankton are typically measured in terms of reductions in growth rates. Therefore, toxicity can be produced both by nutritional deficiencies in competing nutrient

metals, and by the accumulation of excess toxic metals, which disrupt the normal metabolism of the cell.

24. Phytoplankton have three ways of reducing toxicity when exposed to excessive concentrations of copper and nickel: production of phytochelatin which binds the metals inside the cells and stores them in a nontoxic form, excretion of organic cellular exudates which chelate copper ions and reduce biovailability, and induction of efflux systems to excrete accumulated metals from the cells.

25. Accumulation of copper and nickel in the aquatic food web depends on uptake from two routes of exposure, water and food. Accumulation can be calculated from the metal uptake rates from water; metal assimilation efficiencies from food; metal elimination rates from the organisms; organism growth rates, consumption rates, and dietary preferences; and metal concentrations in food items.

26. The uptake and elimination rates must consider the effects of metal regulation by the organisms, at least for copper.

27. A steady-state approach can be used to estimate total metal concentrations in different organisms and relative contributions from water and food. Alternatively, a dynamic food web model can be constructed to predict metal concentrations throughout the food web in response to changing exposure conditions, for example, from seasonal variations in the loading and cycling of the metals, or to future projected conditions in the South Bay.

28. Currently, copper and nickel measurements in aquatic organisms in South San Francisco Bay are limited to benthic bivalves.

Table 4-1
Concentration of Copper in Bedded Sediments and in Water Column Particulates During Dry and Wet Seasons, and Hypothetical Equilibrium Partition Coefficients

| | Copper Concentration (mg/kg) | | | | Hypothetical Equilibrium Partition Coefficient (L/kg) | |
| | Bedded Sediments | | Water Column Particulates | | | |
	Dry	Wet	Dry	Wet	Dry	Wet
STATION						
BA10	37	44	42	38	12,000	12,000
BA20/21	41	49	47	52	13,000	18,000
BA30	41	44	44	53	14,000	20,000
BA40/41	40	46	37	57	15,000	27,000
BB15	31	32	69	81	30,000	44,000
BB30	36	39	60	67	35,000	42,000
BB70	39	44	60	62	34,000	38,000

Dry = dry season
Wet = wet season

Table 4-2
Concentration of Nickel in Bedded Sediments and in Water Column Particulates During Dry and Wet Seasons, and Hypothetical Equilibrium Partition Coefficients

	Nickel Concentration (mg/kg)				Hypothetical Equilibrium Partition Coefficient (L/kg)	
	Bedded Sediments		Water Column Particulates			
	Dry	Wet	Dry	Wet	Dry	Wet
STATION						
BA10	99	126	111	93	24,000	25,000
BA20/21	98	96	114	114	33,000	38,000
BA30	92	83	102	110	35,000	39,000
BA40/41	89	86	86	140	37,000	59,000
BB15	71	68	140	138	67,000	75,000
BB30	83	81	122	106	77,000	64,000
BB70	87	89	159	118	105,000	75,000

Dry = dry season
Wet = wet season

Figure 4-1.   Copper cycling in Lower South San Francisco Bay.
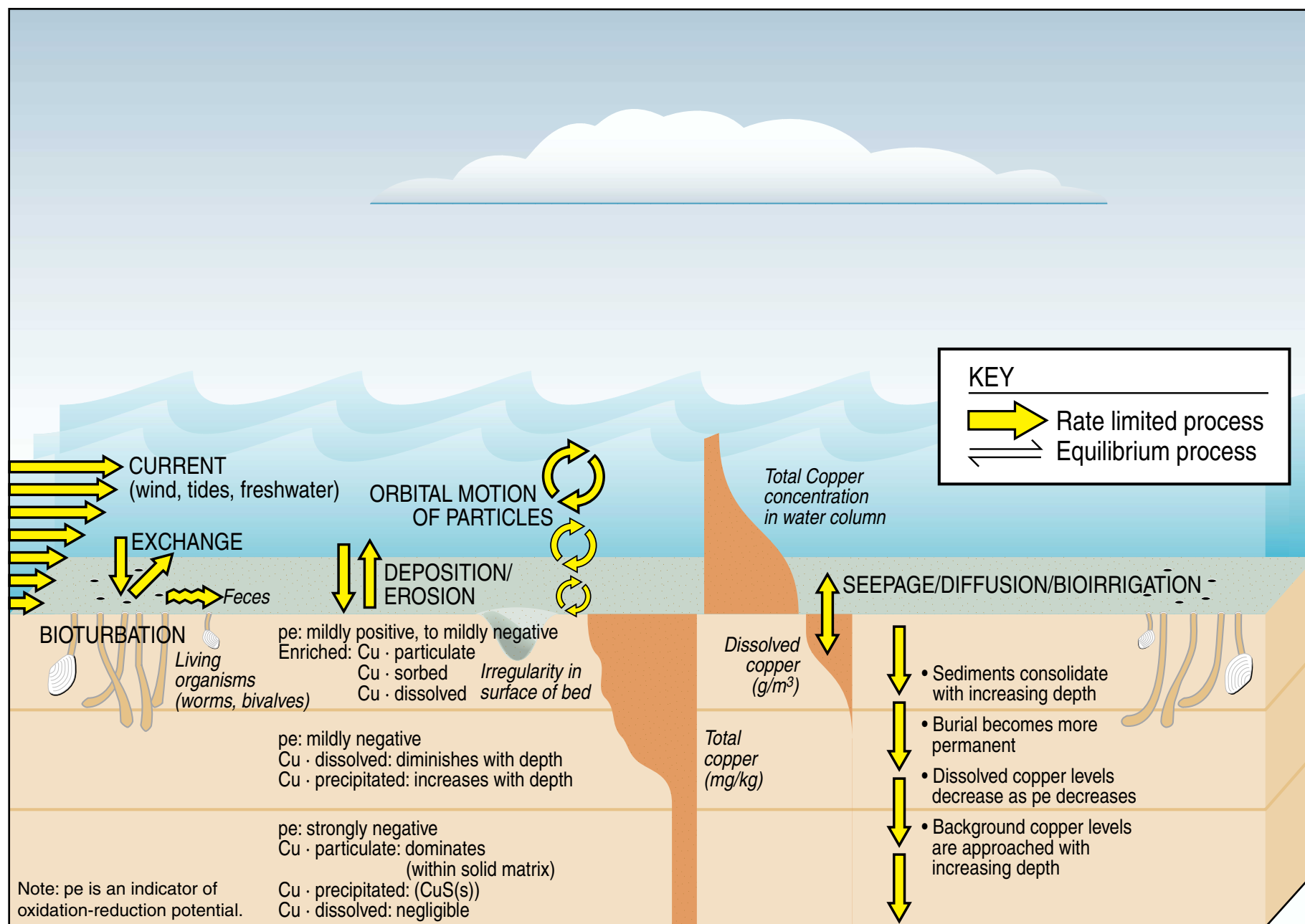
Figure 4-2.   Copper processes in sediment bed.

Figure 4-3.   Nickel cycling in Lower South San Francisco Bay.
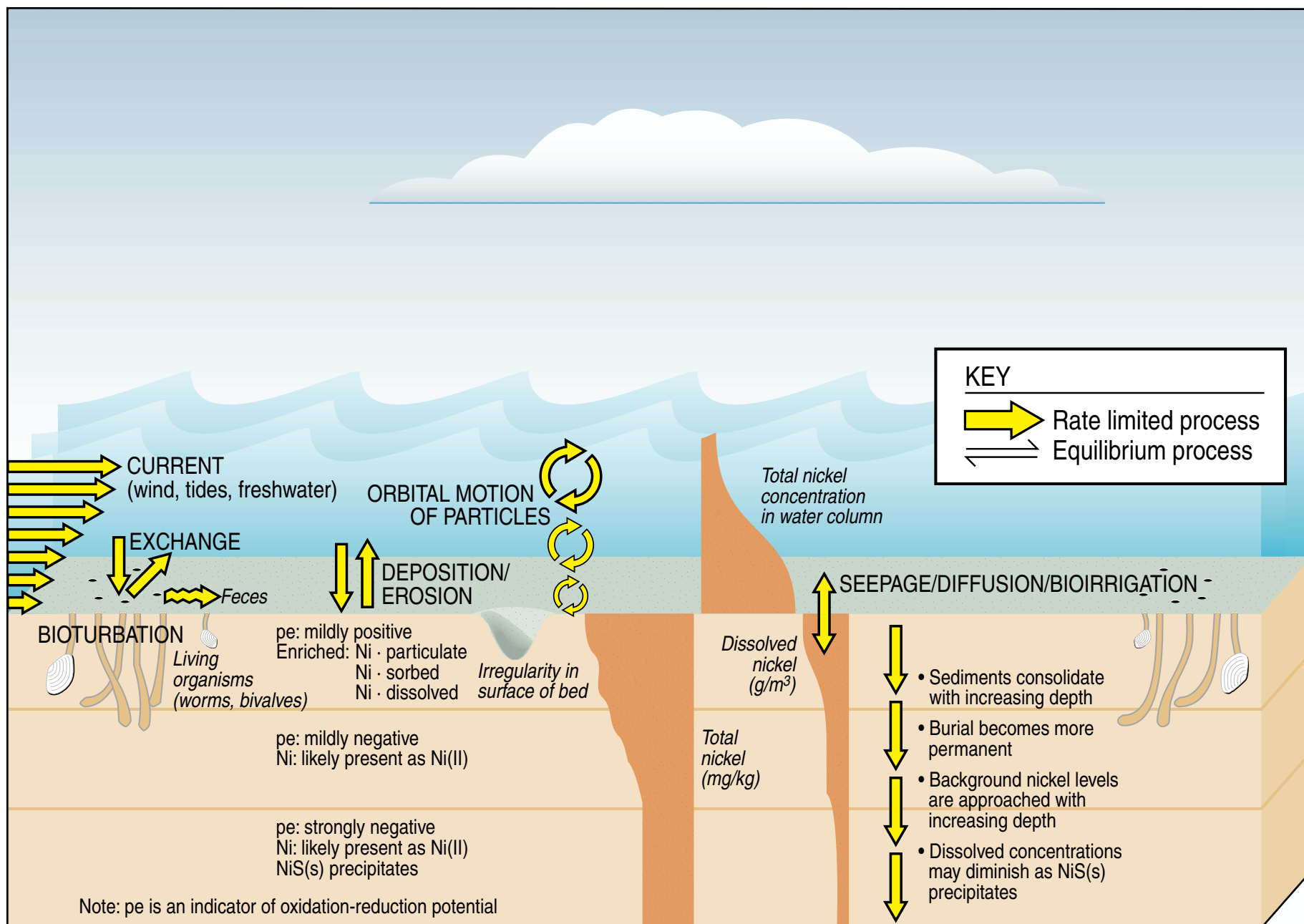
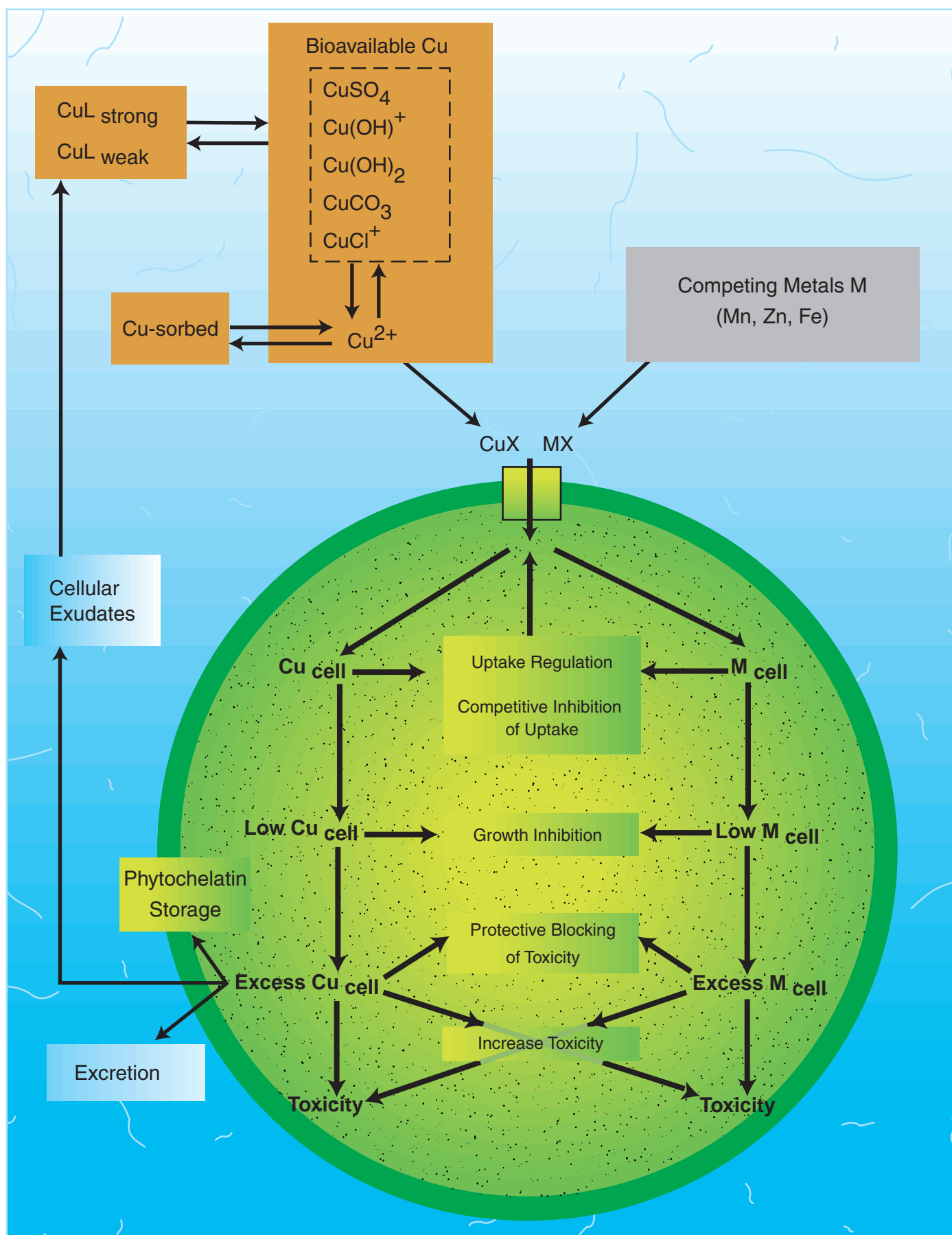Figure 4-4.   Nickel processes in sediment bed.

Figure 4-5.   Copper uptake and toxicity in phytoplankton.

5 CONCEPTUAL MODEL OF FORCING FUNCTIONS THAT INFLUENCE FATE OF COPPER AND NICKEL

5.1 Description

Forcing functions, as used here, are those processes that have a major influence on the fate of copper and nickel in the system, and are, to a large degree, uncontrollable by humans, but must be accounted for so that appropriate TMDLs can be developed. The forcing functions then become the driving forces that must be quantified since they strongly influence other components of the conceptual model, such as nonpoint source loading rates on copper cycling during windy conditions. The major forcing functions identified are illustrated in Figures 5-1 and 5-2, and are tidal forcing, meteorological forcing, hydrologic forcing, and winds. While forcing functions are not necessarily all independent of each other (e.g., stream flow rates are influenced by meteorological events), nevertheless, it is appropriate to discuss each forcing function individually.

Based on the definition of forcing functions provided above, the bathymetry of the Bay can also be considered a forcing function. The bathymetry has a great influence on how the water flows within the Bay, on sediment transport, on flushing, and ultimately on the fate of copper and nickel. More details of the bathymetry of Lower South San Francisco Bay have been presented previously in Sections 2 and 3, and are not repeated here.

Another forcing function has already been implicitly examined, and that is the influence of humans on the watershed that surrounds Lower South San Francisco Bay (and the entire Bay, to a lesser extent). Examples include ongoing urban growth or previous mining activities. Humans have also filled wetlands and other areas around the Bay to create locations for new communities, and continually dredge the Bay (Conomos 1979). As mentioned previously, the conceptual model of Lower South San Francisco Bay does not include the watershed itself, but treats loadings that originate within the watershed as indicative of the forcing associated with the watershed.

As shown in Figure 5-1, tidal forcing is manifested by tides that enter San Francisco Bay through the Golden Gate. Example time series of tidal elevations are illustrated in Figure 5-1 for two time periods: three days and thirty days. The purpose of showing the two time series is to illustrate that multiple tidal frequencies (or alternatively multiple tidal periods) exist that originate from astronomically generated forces. Over a time period of several days, the semi-diurnal and diurnal nature of the tides is evident. Over a time period of approximately one day, two high tides of unequal height and two low tides of unequal height occur. The tidal cycle continues to evolve throughout the month, also shown in the figure, as spring and neap tides occur. Spring tides are those tides that are associated with the largest tidal amplitude, and neap tides are associated with the smallest amplitudes. Typically, as tidal amplitudes change, so do tidally generated velocities. Increased tidal flushing is associated with spring tide conditions, and minimal flushing is associated with neap tide conditions. These conditions affect the flushing of copper and nickel that originate in Lower South San Francisco Bay. Even longer-period tidal components exist, but are not illustrated here.

As the tides propagate into South San Francisco Bay, their propagation and reflection from the end of the Bay can produce a standing wave in South San Francisco Bay, where the amplitude increases with distance from the Golden Gate. An example of this phenomenon is shown in Section 6 of this report.

Freshwater enters San Francisco Bay primarily through the Delta area, and secondarily through local streams that discharge into Lower South San Francisco Bay, and elsewhere within the local watershed (see Figure 5-1). As might be expected due to the relative sizes of the watersheds that feed the Delta and Lower South San Francisco Bay (see Figures 2-5 and 2-8, respectively), the Delta flow rates are enormous, typically orders of magnitude higher than local inflow rates (see Section 6).

The hydrographs are strongly seasonally variable, with peak flows from the Delta occurring during the wet season, and into spring when snowmelt from the distant Sierra Nevada Mountains can further swell the Sacramento and San Joaquin rivers. Peak flows from the local watersheds occur shortly following storm events, since the local snow pack is typically minimal. The many reservoirs in the Lower South San Francisco Bay watershed also mitigate runoff.

Storm events provide the precipitation that ultimately dictates surface water flow rates. Local storms that provide precipitation both directly within the local watershed and within the Sacramento-San Joaquin watershed ultimately contribute stream flow to the Bay, as described above.

The effects of Lower South San Francisco Bay stream inflow rates are to facilitate flushing of copper and nickel out of that portion of the Bay. However, loading rates also increase concomitantly (during wet weather), so that concentrations of copper and nickel might not respond as expected based only on flushing considerations. See Section 6 for a comparison between dry and wet weather concentrations.

In Figure 5-2, an example wind pattern across the Bay is shown. This particular wind pattern is typical of summertime conditions. Several relevant influences of wind are shown in the figure. One is that high sustained wind speeds generated during storm events can strongly influence the tides, so that both astronomical and meteorological tidal influences are important. Another is that, since much of Lower South San Francisco Bay is shallow, as previously shown in Figure 3-5, winds that blow over that portion of the Bay produce wind-generated currents that can resuspend bottom sediments containing copper and nickel. Thus winds, along with tidally generated currents, are important forcing functions with respect to their influence on bedded sediments.

Figure 5-3 illustrates various time scales that are associated with relevant forcing functions. Note that tidal cycle time scales are divided into shorter-term tidal cycles (up to a month) that have been described previously, and longer-term tidal cycles. Astronomically generated tides have frequencies with return periods of about 19 years. Storm events are typically of short duration (less than a day to a week), but certain extreme events can occur very infrequently that may be significant (for example, El Niño events). Ultimately, climatic changes can be influential (for example, sea level changes) but are not relevant here.

5.2   Summary

1. The forcing functions discussed in this section include: tidal forcing, meteorological forcing, hydrological forcing, winds, and bathymetry. The forcing functions all influence the fate of copper and nickel, and are typically not within the control of humans, but are naturally occurring phenomenon (a partial exception is hydrologic forcing: by diverting flow and building dams, surface water inflow rates can be altered).

2. The influence of each forcing function can change both spatially and temporally, and so their relative importance changes accordingly. The bathymetry is the most constant of the forcing functions, but even bathymetry can slowly change over time.

3. During the dry season, tidal forcing, winds, and bathymetry are the dominant forcing functions. During the wet season, all forcing functions exert their influence.
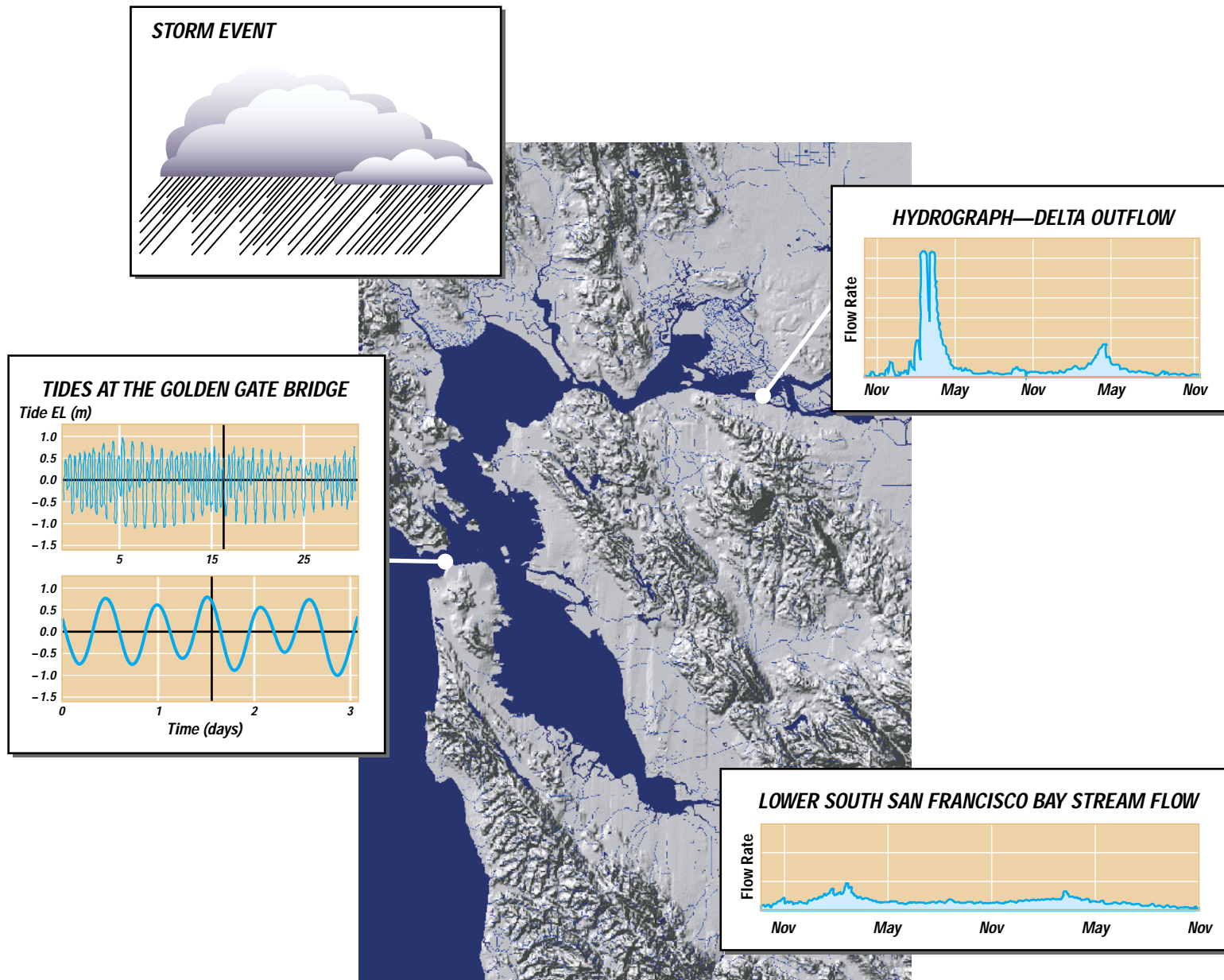
Figure 5-1. Illustration of tidal, freshwater and meteorological forcing functions.

Wind influences tidal elevations

Wind-generated waves in shallow water resuspend bottom sediments

WIND SPEED (knots) AT 10 METERS ABOVE SURFACE

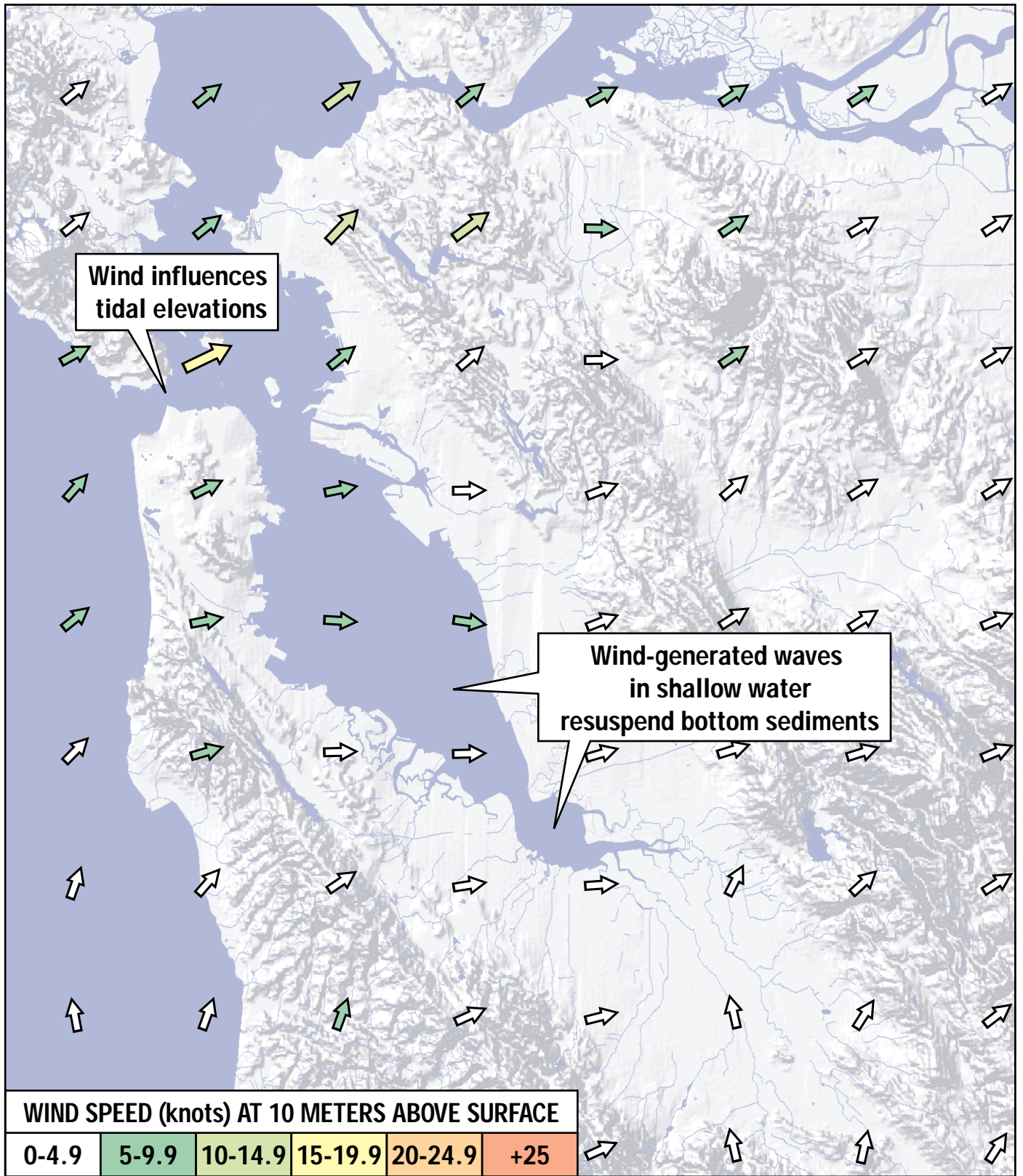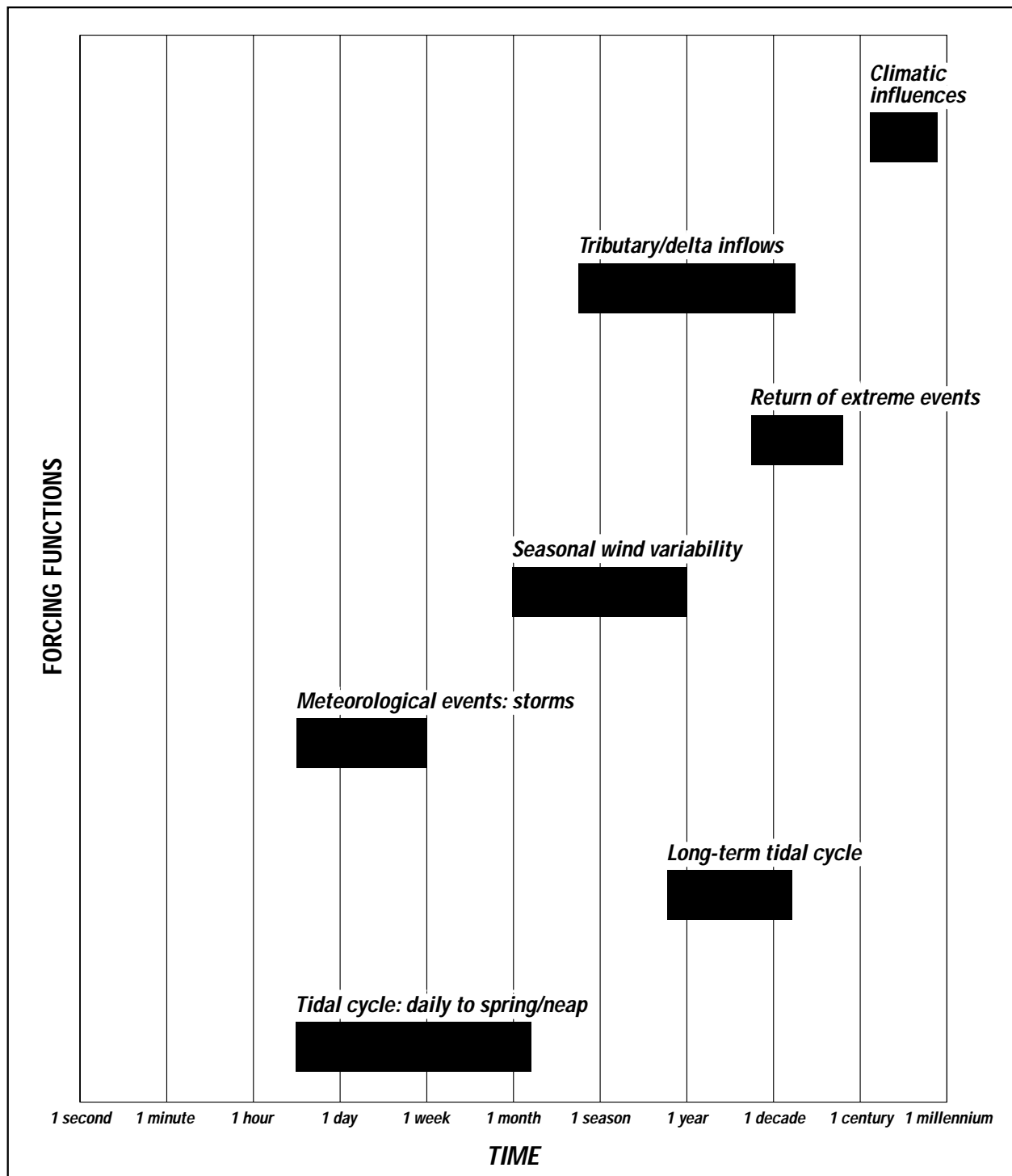| 0-4.9	5-9.9	10-14.9	15-19.9	20-24.9	+25

Figure 5-2. Illustration of wind as a forcing function.

Figure 5-3. Time scales associated with forcing functions.